Notes

Composition of Eucalyptus Oils

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The characteristic composition of imported eucalyptus oils, Cineol type and citronellal type, were investigated by GC and GC-MS. In cineol type eucalyptus oils, cineol; 82～97%, monoterpene hydrocarbons; 6～12%, monoterpene alcohols (pinocarveol, α-Terpineol etc.); 1～4% and in citronellal type oil, citronellal; 67～76% were contained.

Compared with cineol type eucalyptus virgin oil in Japan, all of imported cineol type oils were not contained sesquiterpenoids and a portion of mono terpene hydrocarbons, then it was suggested that cineol content was increased by redistillation in imported cineol type eucalyptus oils.

A small amount of borneol and camphor were found out in one of the imported cineol type eucalyptus oils.

- Received Sep. 7, 1982 -

1. Introduction

It is known that there are various types of eucalyptus oils classified by their main component such as Cineol type, piperidone/phellandrene type, geraniol acetate type and citronellal type.[1)2)] Eucalyptus oils currently imported to Japan are mostly cineol type and rarely are citronellal type. The same cineol type eucalyptus oils may vary in cineol content and other composition depending on the kinds of wood from which they are taken. Namely, the composition of cineol type oil obtained from E. globulus, which is most popular are [3)4)] cineol: 58 to 60%, alphapinene, limonene, p-cymene and other monoterpene hydrocarbons: 8 to 9%, containing in addition some pinocarveol, alpha-terpinoel and other monoterpene alcohols, sesquiterpene alcohols and terpenketones. On the other hand, eucalyptus oils obtained from E.polypractea have the highest cineol content of nearly 90%, other components being p-cymene and other monoterpene hydrocarbons and phenolse.[1)2)] Thus the oils obtained from these two sources differ in composition. Despite such difference, all eucalptus oils are regarded as the same one so long as the tariff list is concerned.

The authors examined the characteristic composition of several types of recently imported eucalyptus oils to aid analysis and identification wqork for tariff list classification. The results are presented in the following.

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2. Experiment

2.1 Samples

Table 1 lists the samples used. Of these, the sample produced in Japan was virgin oil obtained by distilling Eucalyptus binialys (taken at Matsudo) with steam.

Table 1 Samples

Cineol Type	Eucalyptus oil	(Japan)
	〃	(Spain)
	〃	(U.S.A.)
	〃	(China)
Citronellal Type	Eucalyptus citriodora oil	(Brazil)
	〃	(China)

2.2 Sampling thin layer chromatography

The hydrocarbons and oxygen-compounds in the samples were separated by developing in petrol ether using PLC silica gel plate (Merck) as the carrier.

2.3 Gas chromatography

Apparatus: Shimazu GC-7A

Conditions: Column; PEG-20M, 5% on Chromosorb GAW-DMCS 80 to 100 mesh, 2m x 3mm dia.

Column temperature; 80℃ held for 1 minute, increased 240℃ at late of 4℃/min.

Inlet temperature; 250℃

Carry gas; He, 50ml/min.

Detector; FID

2.4 GC-MS

Apparatus: Shimazu LKB-9000, GC-MASPAC 300

Conditions: Ionization voltage; 50eV

Ion current; 60uA

Ion source temperature; 270℃

CG conditions were approximated to gas chromatography conditions.

3. Results and Discussion

3.1 Gas chromatograms of eucalyptus oils

Fig.1 shows the gas chromatograms o cineol-eucalyptus oils and Fig.2 shows those of cintronellal-eucalyptus oils. Peak identification was made using gas chromatography by GC-MS and standard addition method. Chemical composition (%) of the oils determined from relative area of gas chromatograms are listed in Table 2.

The gas chromatograms of cineol-eucalyptus

Table 2 Chemical Composition(%) of Eucalyptus Oils

Origin / Compound	Japan	U.S.A.	Spain	China	China	Brazil
Cineol	68.5	89.3	91.8	87.0	0.4	0.5
Monoterpen hydrcarbon	15.9	6.1	6.1	11.8	1.0	1.2
Sesquiterpene hydrocarbon	2.8	–	–	–		
Monoterpene alcohol	5.5	3.8	1.3	–	18.1	12.4
Sesquiterpene alcohol	6.6	–	–	tr.	1.9	3.8
Citronellal	–	–	–	–	66.7	76.1

This values are for the identified compounds.

oils (Fig.1) are characterized by almost no presence of sesquiterpene alcohols and sesquiterpene hydrocarbons in imported oil samples.

On the other hand, the gas chromatograms of citronellal-eucalyptus oils (Fig.2) have characteristic pattern with the highest peak at citronellal. Both Chinese and Brazilian samples gave similar patterns, which were nearly in agreement with published data.[1)2)]

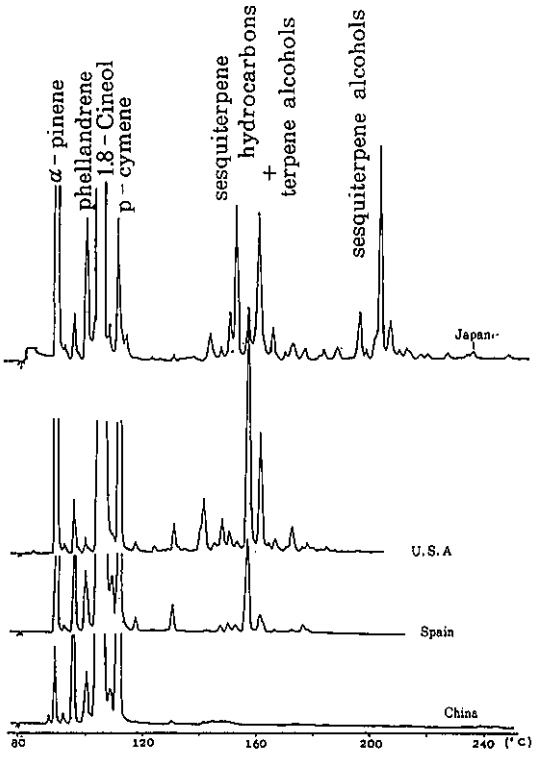

Fig.1 Gaschromatograms of Cineol-Eucalyptus oils

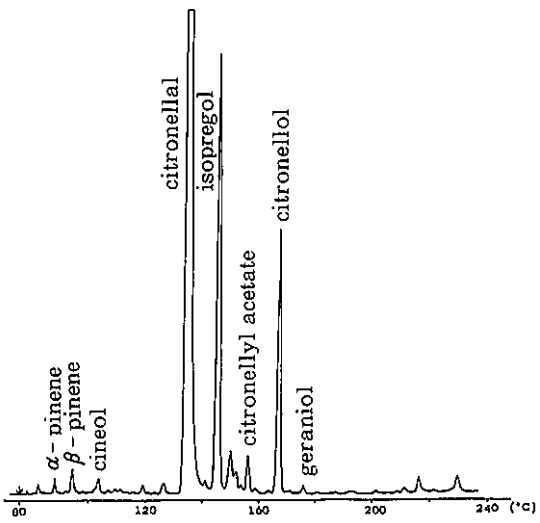

Fig.2 Gaschromtogram of Citronellal-Eucalyptus oil (China)

3.2 Oxygen compounds in cineol-eucalyptus oils

Fig.3 shows the gas chromatograms of oxygen compounds as obtained by thin layer gas chromatography. As can be seen from the figure, the oxygen compounds of the four types of oils are all mainly of pinocarveol and alpha-terpineol and were considered to be from E. globulus. Measurement of the peak corresponding to alpha-terpineol of U.S. sample indicated presence of high peaks at m/e 95 and 110 in addition to mass fragment due to alpha-terpineol. These were considered to be due to mass fragment of borneol in view of the gas chromatogram retention time and peak intensity of cleavage ions (Fig.4). Camphor was also detected in this sample. Borneol and camphor were not reported as components of eucalyptus oils but their detection together with cineol in oils of Baekea plant which is of the same familiy as eucalyptus reported by other worker [1)] and their small content detected in the present work suggest that these were natural ones rather than added ones. The U.S. sample also contained 2-phenyl ethyl alcohol but it was impossible to determine whether it was added one due to too small amount.

From the fact that imported oils (probably from E. globulus) contained almost no sesquiterpenes and that their monoterpene hydrocarbon content was smaller than that of Japanese virgin oil and than

published data [3], these oils imported as cineol-eucalyptus oils were actually not virgin oils. Accoding to literature [2], purified oils obtained from E. globulus have bad smell of low grade aldehydes and hence they are often redistilled to remove such aldehydes and to increase cineol content. It is likely that these imported samples had also been processd similarly to remove low boiling point and high boiling point fractions.

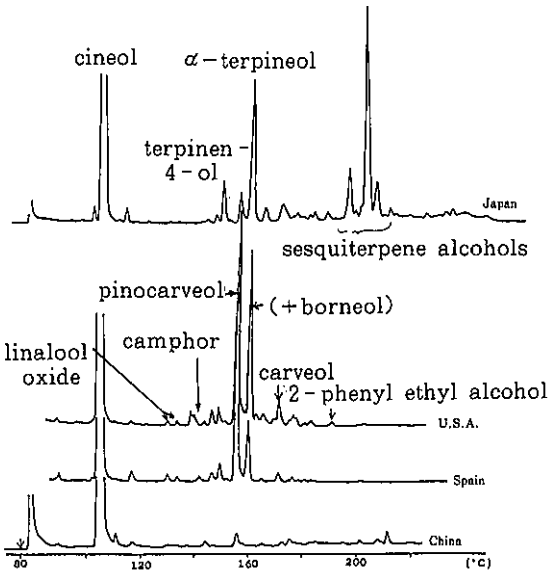

Fig. 3 Gaschromatograms of oxygen compounds in Cineol－Eucaryptus oils

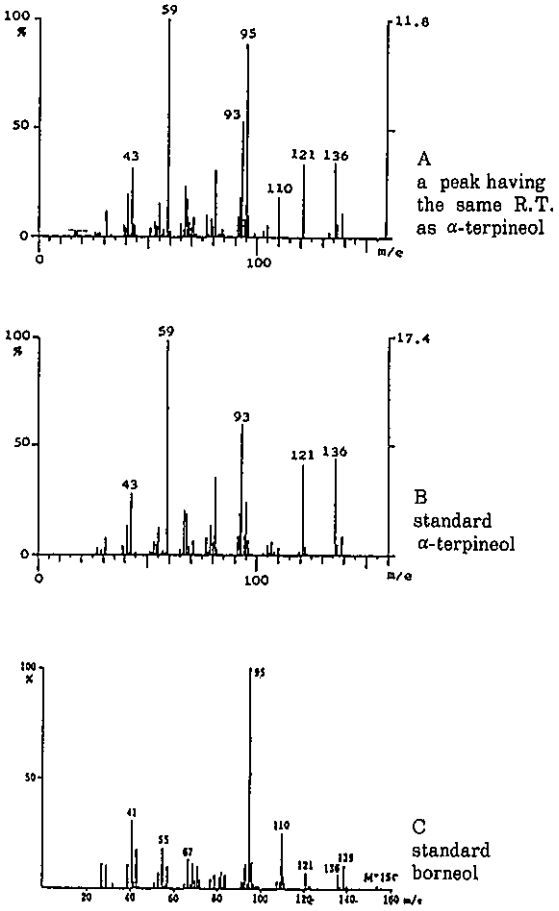

Fig. 4 Mass spectra of A . B , C.

4. Summary

The characteristic composition of recently imported cineol- and citronellal-eucalyptus oils was investigated and it was estimated that the oils imported as cineol-eucalyptus oils would have been subjected to removal of low and high boiling point fractions from virgin oils and to increase in cineol content. In some cineol-eucalyptus oils tested, trace amounts of borneol and camphor whose presence in these oils had not been reported were detected.

References

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